

*Application for*  
**UNITED STATES LETTERS PATENT**

*Of*

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*For*

**PROCESS AND APPARATUS FOR REMOVING RESIDUES FROM THE  
MICROSTRUCTURE OF AN OBJECT**

PROCESS AND APPARATUS FOR REMOVING RESIDUES  
FROM THE MICROSTRUCTURE OF AN OBJECT

BACKGROUND OF THE INVENTION

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This application is a continuation-in-part application of the Japanese Patent Application No. 2001-034337 filed on February 9, 2001.

Field of the Invention

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The present invention relates to a process and an apparatus for removing residues from the microstructure of an object. The present invention specifically relates to a process and an apparatus for removing residues, such as resists, generated during a semiconductor manufacturing process from a semiconductor wafer surface having a fine structure of convex and concave portions.

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Description of the Related Art

It is required as one step in manufacturing a semiconductor wafer to remove residues, such as photoresists, UV-hardened resists, X-ray hardened resists, ashed resists, carbon-fluorine containing polymer, plasma etch residues, and organic or inorganic contaminants from the other steps of the manufacturing process. The dry and wet removal methods are commonly used. In the wet removal method, the semiconductor wafer is dipped in an agent, such as a water solution, including a remover to remove residues from the surface of semiconductor wafer. Recently, supercritical CO<sub>2</sub> is used as such an agent because of its low viscosity.

However, supercritical CO<sub>2</sub> is not enough by itself to remove several residues from the surface of the semiconductor wafer. To resolve this problem, several additives to supercritical CO<sub>2</sub> are proposed. As described in the Japanese unexamined patent publication No. 10-125644, methane or surfactant having CF<sub>x</sub> group is used as an additive to supercritical CO<sub>2</sub>. In Japanese unexamined patent publication No. 8-191063,

dimethylsulfoxide or dimethyl-formamide is used as such an additive. These additives are not always effective for removing residues.

#### SUMMARY OF THE INVENTION

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An object of the present invention is, therefore, to provide a process and an apparatus for effectively removing residues from the microstructure of an object.

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According to the present invention, a process is provided for removing residues from the object, which comprises steps of preparing a remover including a CO<sub>2</sub>, an additive for removing the residues and a co-solvent for dissolving said additive in said CO<sub>2</sub> at a pressurized fluid condition, and bringing the object into contact with said remover so as to remove the residues from the object.

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A process is further provided for removing residues from the microstructure of an object, which comprises a step of contacting the object with a remover including a supercritical CO<sub>2</sub>, a compound having hydroxyl group, and a fluoride of formula NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>F, where R represents a hydrogen or alkyl group.

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An apparatus is further provided for removing residues from the object, which comprises a vessel, at least one inlet for feeding into said vessel a CO<sub>2</sub>, an additive for removing the residues and a co-solvent for dissolving said additive in said CO<sub>2</sub>, a pump for pressurizing CO<sub>2</sub> into said vessel, and a heater for keeping said pressurized CO<sub>2</sub> at a predetermined temperature.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and additional features and characteristics of the present invention will become more apparent from the following detailed description considered with reference to the accompanying drawings in which like reference numerals designate like elements and wherein:

FIG. 1 is a schematic diagram of an apparatus for removing residues in accordance with the present invention.

5 FIG. 2 is a schematic diagram of another embodiment of the apparatus for removing residues in accordance with the present invention.

FIG. 3 shows an effect of the concentration of tetramethylammoniumfluoride (hereinafter referred to as "TMAF") on the etch rate.

10 FIG. 4 shows an effect of the concentration of ethanol on the etch rate.

FIG. 5 is a schematic diagram of a third embodiment of the apparatus for removing residues in accordance with the present invention.

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#### PREFERRED EMBODIMENTS OF THE INVENTION

The present invention is applied to the microstructure of an object, e.g., a semiconductor wafer having a fine structure of convex and concave portions on its surface, and a 20 substrate made of a metal, plastic or ceramic which forms or remains continuous or non-continuous layer of materials different therefrom.

As the pressurized CO<sub>2</sub> is not enough by itself to remove residues, the pressurized CO<sub>2</sub> of the present invention, to which an additive and a co-solvent are added, is used as a 25 remover for removing residues from the object. The additive used for this purpose can remove residues but cannot substantially dissolve in CO<sub>2</sub> by itself. The co-solvent used for this purpose can make the additive dissolved or dispersed homogeneously in CO<sub>2</sub>.

The pressurized CO<sub>2</sub> has a high dispersion rate and enables the dissolved residues to 30 disperse therein. If CO<sub>2</sub> is converted to a supercritical condition, it penetrates into fine pattern portions of the object more effectively. By this feature, the additive is conveyed into pores or concave portions on a surface of the object due to the low viscosity of

$\text{CO}_2$ . The  $\text{CO}_2$  is pressurized to 5 MPa or more, but not less than 7.1 MPa at a temperature of 31°C to convert the  $\text{CO}_2$  to a supercritical fluid condition.

The basic compound is preferably used as the additive because it effectively hydrolyzes polymers typically used as a resist in manufacturing a semiconductor. The preferred basic compound includes at least one element selected from the group consisting of quaternaryammoniumhydroxide, quaternaryammoniumfluoride, alkylamine, alkanolamine, hydroxylamine, and ammoniumfluoride. It is preferred to use a compound including at least one of quaternaryammoniumhydroxide, quaternaryammoniumfluoride, hydroxyammine and ammoniumfluoride to remove novolac phenol resists from a semiconductor wafer. The quaternaryammoniumhydroxide may be any quaternaryammoniumhydroxide, e.g. tetramethylammoniumhydroxide, tetraethylammoniumhydroxide, tetrapropylammoniumhydroxide, tetrabutylammoniumhydroxide (hereinafter referred as TBAH), and choline. The quaternaryammoniumfluoride may be any quaternaryammoniumfluoride, e.g. tetramethylammoniumfluoride (hereinafter referred as TMAF), tetraethylammoniumfluoride, tetrapropylammoniumfluoride, tetrabutylammoniumfluoride, and cholinefluoride. The alkylamine may be any alkylamine, e.g. methylamine, dimethylamine, ethylamine, diethylamine, triethylamine, and propylamine, dipropylamine. The alkanolamine may be any alkanolamine, e.g., monoethanolamine, diethanolamine, and triethanolamine.

The additive is preferably added in a ratio of not less than 0.001 wt. % of the remover, more preferably in a ratio of not less than 0.002 wt. %. When the additive is added in a ratio of more than 8 wt. %, the co-solvent should be added more, but the amount of  $\text{CO}_2$  is decreased according to the amount of the added co-solvent, which decreases the penetration of  $\text{CO}_2$  into a surface of the object. The upper range of the additive is 8 wt. %, preferably 6 wt. %, and more preferably 4 wt. %.

According to the present invention, the co-solvent is added to  $\text{CO}_2$  together with the additive. The co-solvent of the present invention is a compound having an affinity to both  $\text{CO}_2$  and the additive. Such a co-solvent dissolves or disperses the additive

homogeneously in the pressurized CO<sub>2</sub> in fluid condition. An alcohol, dimethylsulfoxide or a mixture thereof is used as the co-solvent. The alcohol may be any alcohol, e.g. ethanol, methanol, n-propanol, iso-propanol, n-butanol, iso-butanol, diethyleneglycolmonomethylene, diethyleneglycolmonoethylene, and hexafluoro isopropanol, preferably ethanol and methanol.

The kind and amount of the co-solvent are selected depending on the kind and amount of the additive to CO<sub>2</sub>. The amount of the co-solvent is preferably five times or more than that of the additive because the remover easily becomes homogeneous and transparent. Alternatively, the remover may include the co-solvent in a range of 1 wt. % to 50 wt. %. If more than 50 wt. % of the co-solvent is added, the penetration rate of the remover decreases due to less amount of CO<sub>2</sub>. It is preferable to use a remover including CO<sub>2</sub>, alcohol as the co-solvent, quaternaryammoniumfluoride and/or quaternaryammoniumhydroxide as the additive because these additives are well dissolved in CO<sub>2</sub> by alcohol and are CO<sub>2</sub>-philic.

According to the present invention, it is preferable to contact the object with a remover composed of CO<sub>2</sub>, a fluoride of formula NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>F, (R represents a hydrogen or alkyl group), and a compound having hydroxyl group, while CO<sub>2</sub> is high pressurized or is preferably kept at a supercritical condition. This remover is more effective to remove ashed residues from the semiconductor wafer. The fluoride may be any fluoride of formula NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>F where R represents a hydrogen or alkyl group, e.g. ammonium fluoride, tetramethylammoniumfluoride, and tetraethylammoniumfluoride. It is preferable to use the fluoride with R<sub>s</sub> being alkyl groups, such as tetramethylammoniumfluoride and tetraethylammoniumfluoride because such fluorides are CO<sub>2</sub>-philic. In the present invention, the remover may include the fluoride preferably in the range from 0.001 wt % to 5 wt % of the remover, more preferably in the range from 0.002 wt % to 0.02 wt % of the remover.

The fluoride is used as the additive to supercritical CO<sub>2</sub> in the presence of a compound having a hydroxyl group, e.g., alcohol (such as ethanol, methanol, n-propanol, isopropanol, n-butanol and isobutanol, phenol), glycol (such as ethyleneglycol and

methylenglycol and polyethylenglycol). The alcohol is preferred because it effectively dissolves or disperses the fluoride, such as TMAF, homogeneously in supercritical CO<sub>2</sub>. Among alcohol, ethanol is preferable because a larger amount of the fluoride, such as TMAF, can be dissolved in supercritical CO<sub>2</sub> by the presence of the ethanol. The concentration of the compound in supercritical CO<sub>2</sub> depends on the kind and concentration of the fluoride, and the kind of the residue. Approximately, the compound is preferably included in supercritical CO<sub>2</sub> in the range from 1 wt % to 20 wt % of the remover.

- 5 10 It is preferable that the supercritical CO<sub>2</sub> further comprises dimethylacetamide (hereinafter referred to as "DMAC"). The DMAC contained in the CO<sub>2</sub> is preferably six to seventy times of the fluoride contained in the CO<sub>2</sub> by weight. Further, it is preferable that the supercritical CO<sub>2</sub> includes substantially no water, which is a hindrance for manufacturing semiconductor wafers.

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Figure 1 shows a simplified schematic drawing of an apparatus use for removing residues according to the present invention. Firstly, the semiconductor wafer having residues on its surface is introduced to and placed in a high pressure vessel 9, then CO<sub>2</sub> is supplied from a CO<sub>2</sub> cylinder 1 to the high pressure vessel 9 by a high pressure pump

- 20 2. The high pressure vessel 9 is thermostated at a specific temperature by a thermostat 10 in order to maintain the pressurized CO<sub>2</sub> in the high pressure vessel 9 at the supercritical condition. An additive and a co-solvent are supplied to the high pressure vessel 9 from tanks 3 and 6 by high pressure pumps 4 and 7, respectively, while the additive and co-solvent are mixed by a line mixer 11 on the way to the high pressure vessel 9. The flow rates of the additive and the co-solvent are adjusted by valves 5 and 8, respectively in order to set to the predetermined values. The CO<sub>2</sub>, the additive and the co-solvent may be supplied continuously.
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- 30 Figure 2 shows another embodiment of the apparatus for removing residues according to the present invention. In this apparatus, the additive is mixed with the co-solvent by the line mixer 11 before being fed into the high pressure vessel 9 in order to avoid heterogeneously contacting. The ratio of the additive and the co-solvent to be fed into

the high pressure vessel 9 is controlled by a ratio controller 12, which regulates the feeding rate(s) of the additive and/or the co-solvent to the supercritical CO<sub>2</sub> in the high pressure vessel 9.

- 5 The removing process is performed at a temperature in the range from 31°C to 210°C, and at a pressure ranged from 5 M Pa to 30 M Pa, preferably, from 7.1 M Pa to 20 M Pa. The time required for removing the residues depends on the size of the object, the kind and amount of the residues, which is usually in the range from a minute to several ten minutes.

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Hereinafter, the present invention is described with reference to experiments.

### EXPERIMENT 1

- 15 This experiment is carried out by dipping an object in an additive shown in table 1 at an atmospheric pressure at a temperature in the range of from 40°C to 100°C for 20 minutes. The object for this experiment is a silicon wafer having a SiO<sub>2</sub> layer coated with a novolac phenol type resist, patterned by a development, and treated to form microstructures on its surface by dry etching of a fluorine gas. A rate of removing  
20 residues is estimated as a ratio of an area of the surface adhering with residues after removing and before removing by a microscope. The term “x” and the term “O” mean that the rate is less than 90%, and 90% or more, respectively. The term “Ø” means the rate is 90% or more when the additive is diluted ten times by a co-solvent such as dimethylsulfoxide.

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The results are summarized in table 1.

Table 1

Additive	Removability
Acetone	x
Dimethylformamide	x
Dimethylsulfoxide	x
N-methyl-2-pyroridon	x
Propylencarbonate	x
Methylamine	O

Ethylamine	O
Monoethanolamine	O
Hydroxytetramethylammonium solution*	Ø
Choline solution**	Ø
Hydroxylamine solution***	Ø
Ammonium fluoride solution****	Ø

\*Hydroxytetramethylammonium solution (ethanol) includes 25% of hydroxytetramethylammonium.

\*\*Choline solution (water) includes 50% of choline.

\*\*\*Hydroxylamine solution (water) includes 50% of hydroxylamine.

- 5 \*\*\*\* Ammonium fluoride solution (water : dimethylformamide = 1:9) includes one percent of ammonium fluoride.

As shown in table 1, alkylamine (such as methylamine and ethylamine), alkanolamine (such as monoethanolamine), quaternary ammonium hydroxide (such as TMAH and 10 choline), hydroxylamine, and ammonium fluoride have high removability. Especially, quaternary ammonium hydroxide, hydroxylamine, and ammonium fluoride have a superior rate for removing residues.

## EXPERIMENT 2

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This experiment for investigating an effect of co-solvent on a solubility of additive in CO<sub>2</sub> is carried out via the apparatus shown in Fig. 5. CO<sub>2</sub> is introduced into the vessel 9 from the CO<sub>2</sub> cylinder 1 by the pump 2. The pressure and the temperature in the vessel are maintained at 20 MPa and 80°C by the thermostat 10. The additive and co-solvent 20 are mixed in the ratio shown in table 2, then the mixture is introduced into the vessel 9 from the mixing tank 14 by the pump 4. The same amount of CO<sub>2</sub> as the mixture is evacuated from the vessel 9 so that the pressure is maintained at 20 MPa when the mixture is introduced. The effect of co-solvent, i.e., whether the additive is dissolved in CO<sub>2</sub>, is observed through the glass window 13 of the vessel 9. When the additive is not 25 dissolved in CO<sub>2</sub>, two phases are observed through the window. The term "x" in table 2 means that the two phases are observed. The term "O" means the co-solvent makes the additive dissolved or dispersed homogeneously in CO<sub>2</sub> (the two phases are not

observed).

Table 2

Exp. No.	Additive		Co-solvent		Observation
		wt %		wt %	
2-1	TMAH	1.21	ethanol	22.1	O
2-2	TMAH	1.50	dimethylsulfoxide	30.0	O
2-3	TBAH	0.40	ethanol	38.1	O
2-4	choline	0.05	ethanol	20.0	O
2-5	choline	1.76	ethanol	35.3	O
2-6	choline	0.25	ethanol	24.0	O
2-7	choline	0.29	isopropanol	27.9	O
2-8	choline	0.39	DEGME	38.3	O
2-9	Mono-ethanolamine	0.05	ethanol	25.0	O
2-10	Non		Non		O
2-11	Non		ethanol	20.0	O
2-12	choline	0.05	Non		x

DEGME: diethyleneglycolmethyl ether

5 As shown in table 2, in experiment No. 2-1~2-9, the effects of co-solvents are confirmed. The conditions in experiment No. 2-1~2-9 observed through the window are transparent, homogenous, and without two phases.

### EXPERIMENT 3

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This experiment for removing residues using a remover including high pressure CO<sub>2</sub>, additive(s), and co-solvent(s) is carried out via the apparatus of Fig. 1. The object in this experiment is the same as the one in the experiment 1. The kind and concentration of the additive and co-solvent in the remover are shown in table 3. The terms "O", "O" and "x" in table 3 indicate the rate of removing residues being 90% or more, 60% or

15 more, and 10% or less, respectively.

Table 3

Exp. No.	Additive		Co-solvent		Rate
		Wt%		Wt%	
3-1	Choline	0.05	Ethanol	20.0	O
3-2	Choline	1.70	Ethanol	35.3	O
3-3	TMAH	1.21	Methanol	22.2	O
3-4	TMAH	1.50	Dimethylsulfoxide	30.0	O
3-5	Non		Non		x

3-6	Non	Ethanol	20.0	x
3-7	Non	dimethylsulfoxide	30.0	x

As shown in table 3, in the experiment No. 3-1~3-4, the residues are effectively removed.

## 5 EXPERIMENT 4

This experiment for removing residues from the surface of semiconductor wafers is carried out by using a remover including additives H, I, G, J, L, and K which include the fluoride of formula NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>F (R represents a hydrogen or alkyl group). The compositions of the additives are listed in Table 4.

Table 4 Compositions of Additive

Additive	Fluoride (wt % of additive)	Other components (wt % of additive)	
H	TMAF (13.43)	DMAC (62.5)	DIW (24.07)
I	TMAF (4.48)	DMAC (67.5)	DIW (28.02)
G	NH4F (5.0)	DMAC (64.2)	DIW(12.4), AcOH (8.0 ), NH4OAc (10.4)
J	TBAF (25)	DMAC (43)	Ethanol (32)
L	TBAF (32)	DMAC (39)	Ethanol (29)
K	TMAF (5)	DMAC (62.5)	Ethanol (32.5)

DMAC:Dimethylacetamide, DIW:De-ionized water, TMAF: Tetramethylammoniumfluoride, PG: Propyleneglycol, DMSO: Dimethylsulfoxide, AcOH: Acetic acid, TBAF: Tetrabutylammoniumfluoride, NH4OAc: ammonium acetate.

In this experiment, three kinds of silicon wafers A, B and C are used. These silicon wafers have different patterns on their surfaces and the removing characteristics of their resists are also different. The silicon wafers are prepared to generate the thermal oxides of silicon on the surface thereof and broken into chips (1cm x 1cm). The chips are etched in the fluoride gas. Then the resists on the chips are ashed by a plasma to generate ashed resists. The chips are placed in the high pressure vessel 9. The solutions of additives H, I, G, J, K and L are prepared such that the fluoride is dissolved in the other components listed in the table 4, respectively. Then, such additives are introduced with CO<sub>2</sub> and ethanol into the high pressure vessel in Fig. 1. The temperature of CO<sub>2</sub> in the high pressure vessel 9 is 40°C, the pressure is 15 M Pa, and the time for making the

chips contact with CO<sub>2</sub> is 3 minutes. After taken out from the high pressure vessel 9, the chips are observed with an electron microscope.

The result of this experiment is summarized in Table 5.

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Table 5

Run	Wafer	Additive	Conc. in Remover [wt%]		Result
			Additive	Ethanol	
1	A	H	0.05	5	Excellent
2	A	I	0.05	5	Excellent
3	B	H	0.05	5	Fair
4	B	H	0.10	5	Excellent
5	B	H	0.25	5	Fair
6	B	I	0.05	5	Fair
7	C	H	0.10	5	Excellent
8	A	G	0.05	5	Fair, but water rinse needs to remove the residue newly appeared
9	A	J	0.05	5	Excellent
10	A	K	0.05	5	Excellent
11	A	L	0.05	5	Excellent
12	B	J	0.10	5	Excellent
13	B	K	0.10	5	Excellent
14	B	L	0.10	5	Excellent

The ashed resists on the wafer-A are cleaned by both 0.05wt% of H and I with 5wt% ethanol dissolved in the supercritical CO<sub>2</sub>. The term "Excellent" means that there is no residues on the surface of the silicon wafer (chips). The term "Fair" means that there are a few residues on the surface or a little disappearance of the pattern. In Run 8 using NH<sub>4</sub>F, a water rinse is needed to remove residue since a water-soluble residue newly appears on the surface of the silicon wafer (chips). In Runs 1 to 7 and 9 to 14, the water rinsing step subsequent to the removing step is not needed. In these cases, a solvent including CO<sub>2</sub> and alcohol, e.g. methanol and ethanol, but no water is preferably used for rinsing the silicon wafer. Further, in cases of the additives J, K and L, no water is substantially needed in both steps of removing and rinsing. Such method is superior because it uses substantially no water which becomes a hindrance for manufacturing semiconductor wafers.

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Wafer-C contains more difficult ashed resists to be removed from the surface of the silicon wafer (chips). In order to remove this resist, longer removing time (three times

longer than wafer-B) is required. The result is excellent.

### EXPERIMENT 5

- 5 The silicon wafers are prepared to generate the thermal oxides of silicon on their surface and are broken into chips. The chips are placed in the high pressure vessel 9 in Fig. 1. Then, a remover including CO<sub>2</sub>, the additives, and ethanol is introduced into the high pressure vessel 9. After the removal treatment for several ten minutes, the chips are taken out and the thickness of the thermal oxides on the chips is measured by an ellipsoimeter. The etch rate of the thermal oxides is determined by dividing the decrease of the thickness per the treatment time. The temperature of CO<sub>2</sub> at the supercritical condition is 40C, the pressure is 15 M Pa, and the treatment time is 20 to 60 minutes.
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- 15 The result of this experiment is summarized in Table 6

Table 6

Additive	Concentration in Remover [wt%]		Etch Rate of thermal oxides of silicon [A/min]
	additive	Ethanol	
H	0.030	5.9	2.4
H	0.047	4.7	4.6
H	0.228	4.3	7.5
I	0.025	5.1	1.4
I	0.044	2.2	3.3
I	0.048	4.8	1.6
I	0.049	4.8	1.6
I	0.050	5.0	1.7
I	0.050	10.0	0.3
I	0.056	5.5	1.6
I	0.057	2.8	2.0
I	0.057	5.6	1.9
I	0.071	3.5	3.7
I	0.248	4.7	5.3
G	0.005	5.1	1.1
G	0.012	4.7	-0.1
G	0.028	5.5	3.9
G	0.039	5.1	8.3
G	0.043	4.2	7.9
G	0.044	4.4	5.1

These data in table 6 are plotted in Figures 3 and 4. As shown in Figure 3, the etch rate of thermal oxides depends on the concentration of additives. Besides, as shown in Figure 4, if the concentration of the additive is constant, the etch rate varies according to the ethanol concentration. The etch rate can be controlled according to the removing objects or the removing process. As seen from Figures 3 and 4, the etch rate is controlled by adjusting the concentrations of the additive and ethanol, and their ratio.

The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. However, the invention which is intended to be protected is not limited to the particular embodiments disclosed. The embodiments described herein are illustrative rather than restrictive. Variations and changes may be made by others, and equivalents employed, without departing from the spirit of the present invention. Accordingly, it is expressly intended that all such variations, changes and equivalents which fall within the spirit and scope of the present invention as defined in the claims, be embraced thereby.